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Allenyl–propargyl tautomerism at palladium(IV) and platinum(IV) centres[1]

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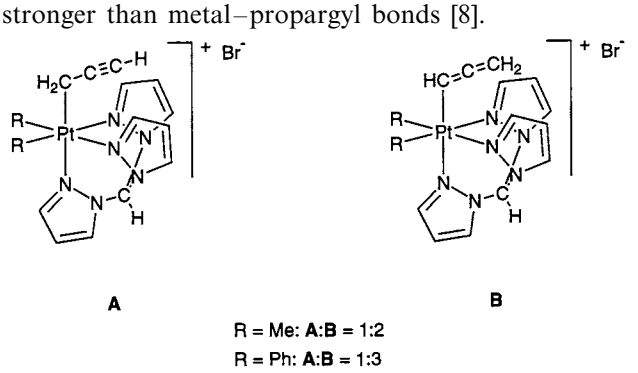
Abstract

The propargylic bromides $MeC{\equiv}CCH_2Br$ and $HC{\equiv}CCH_2Br$ undergo oxidative addition reactions with $[MMe_2\{(pz)_3BH\}]^-$ {M = Pd, Pt; $[(pz)_3BH]^-$ = tris(pyrazol-1-yl)borate}, $[Pd(CH_2CH_2CH_2CH_2)\{(pz)_3BH\}]^-$ and $MMe_2(bpy)$ (M = Pd, Pt; bpy = 2,2′-bipyridine) to form the octahedral metal(IV) complexes $MMe_2(CH_2C{\equiv}CMe)\{(pz)_3BH\}$ [M = Pd (**1**), Pt (**3**)], $Pd(CH_2CH_2CH_2CH_2)(CH_2C{\equiv}CMe)\{(pz)_3BH\}$ (**2**), $Pd(CH_2CH_2CH_2CH_2)(CH{=}C{=}CH_2)\{(pz)_3BH\}$ (**5**), $PdMe_2(CH{=}C{=}CH_2)\{(pz)_3BH\}$ (4), a mixture of tautomers $PtMe_2(CH_2C{\equiv}CH)\{(pz)_3BH\}$ (**6a**) and $PtMe_2(CH{=}C{=}CH_2)\{(pz)_3BH\}$ (**6b**), $MBrMe_2(CH_2C{\equiv}CMe)(bpy)$ [M = Pd (**7**), Pt (**8**)], a mixture of structural isomers $PdBrMe_2(CH_2C{\equiv}CH)(bpy)$ with the propargyl group *trans* to bromine (**9a**) and bpy (**9b**), and a mixture of tautomers and structural isomers for $PtBrMe_2(CH_2C{\equiv}CH)(bpy)$ (**10a**, **10b**) and $PtBrMe_2(CH{=}C{=}CH_2)(bpy)$ (**10c**, **10d**). The preference for adoption of the propargyl or allenyl form is dependent upon metal, ancillary ligands, and substitution in the propargyl/allenyl fragment $M{-}C_3H_3$ and $M{-}C_3H_2Me$: for $M{-}C_3H_2Me$ propargyl is favoured and for $M{-}C_3H_3$ allenyl is favoured for the Pd(IV)/$[(pz)_3BH]^-$ substrates but propargyl is favoured for the Pd(IV)/bpy substrate.

Keywords: Palladium; Platinum; Oxidative addition; Allenyl; Propargyl; 2,2′-Bipyridine; Tris(pyrazol-1-yl)borate

1. Introduction

The synthetic, structural and reaction chemistry of propargyl ($M{-}CR^1R^2{-}C{\equiv}CR^3$) and allenyl ($M{-}CR^3{=}C{=}CR^1R^2$) complexes of palladium [1–8] and platinum [6–16] has developed concurrently with the realisation that such species are involved in organic synthesis procedures employing palladium catalysts, e.g. [19–35]. Complexes are often formed by oxidative adddition reactions of propargyl [1,2,9–11,14–18] or allenyl halides [2,9,15] with metal(0) precursors, and in this chemistry one particular focus of interest has been the tautomerism exhibited by the metal(II) complexes. In this respect, it is of interest that the standard enthalpy of formation of $CH_3{-}C{\equiv}CH$ (184.9 ± 0.8 kJ mol^{-1}) and $CH_2{=}C{=}CH_2$ (190.5 ± 1.2 kJ mol^{-1}) [36] indicate slightly higher stability for the propargyl form, but that metal–allenyl bonds are expected to be stronger than metal–propargyl bonds [8].



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[1] Dedicated to Professor Brian Johnson on the occasion of his 60th birthday.

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$$M^0 \xrightarrow[R^1R^2C{=}C{=}CR^3X]{CR^3{\equiv}C{-}CR^1R^2X\ \text{or}} M^{II}(X)(CR^1R^2{-}C{\equiv}CR^3)\ \text{and/or}\ M^{II}(X)(CR^3{=}C{=}CR^1R^2) \quad (1)$$

$$[MMe_2\{(pz)_3BH\}]^- + RBr \rightarrow MMe_2R\{(pz)_3BH\} + Br^- \quad (2)$$

M = Pd: **1**, **2**, **4**; M = Pt: **3**, **6**

$$[\overline{Pd(CH_2CH_2CH_2CH_2)}\{(pz)_3BH\}]^- + RBr \rightarrow \overline{Pd(CH_2CH_2CH_2CH_2)}R\{(pz)_3BH\} + Br^- \quad (3)$$

(**2**, **5**)

$$MMe_2(bpy) + RBr \rightarrow MBrMe_2R(bpy) \quad (4)$$

M = Pd: **7**, **9**; M = Pt: **8**, **10**

Higher oxidation state complexes are limited to the isolation of a mixture of propargyl (**A**) and allenyl (**B**) tautomers on the oxidative addition of $HC{\equiv}C{-}CH_2Br$ to $PtR_2\{(pz)_3CH\}$ [$(pz)_3CH$ = tris(pyrazol-1-yl)methane] [37]. We report here a study of the synthesis and isomerism of palladium(IV) and platinum(IV) complexes containing the tris(pyrazol-l-yl)borate ligand, $[(pz)_3BH]^-$, which is known to give more stable palladium(IV) complexes than $(pz)_3CH$ [38]. The classical bidentate 2,2′-bipyridine (bpy) as an auxiliary ligand has been included for comparison because of its important role in the development of the higher oxidation state organometallic chemistry of these metals [39,40].

2. Experimental section

The reagents $PdMe_2$(tmeda) (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) [41,42], $Pd(\overline{CH_2CH_2CH_2C}H_2)$(tmeda) [43,44], $PdMe_2$(bpy) [42,45], $PtMe_2$(bpy) [46], $[PtMe_2(SEt_2)]_2$ [46], and $K[(pz)_3BH]$ [47] were prepared as described; other reagents were used as received and solutions of $[PdMe_2\{(pz)_3BH\}]^-$, $[Pd(\overline{CH_2CH_2CH_2CH_2})\{(pz)_3BH\}]^-$ [48] and $[PtMe_2\{(pz)_3BH\}]^-$ [49] were generated as reported. Solvents were dried and distilled, and all procedures were carried out under nitrogen. Microanalyses were by the Central Science Laboratory, University of Tasmania, and NMR spectra were recorded with a Bruker AM 300 spectrometer with chemical shifts given in ppm relative to TMS.

2.1. Synthesis of complexes

2.1.1. $PdMe_2(CH_2C{\equiv}CMe)\{(pz)_3BH\}$ (1)

A solution of $PdMe_2$(tmeda) (0.030 g, 0.120 mmol) and $K[(pz)_3BH]$ (0.030 g, 0.120 mmol) in acetone (10 ml) was stirred for ca. 1 h at 0°C. 2-Butynyl bromide was added and the solution stirred overnight at room temperature. After centrifugation, the pale yellow solution was separated from a white solid and evaporated in a vacuum. The residue was extracted with diethyl ether (2 × 5 ml) and filtered through a Celite column. The solvent was evaporated to dryness and the residue treated with diethyl ether/petroleum ether (b.p. 40–60°C) to give a white crystalline solid (0.035 g, 73%). ^{1}H-NMR ($CDCl_3$): δ 7.66 (d) and 7.53 (m) (6, H3 and H5), 6.20 (m, 3, H4), 2.70 (q, $^5J_{HH}$ = 3.0 Hz, 2, $PdCH_2$), 1.79 (t, $^5J_{HH}$ = 3.0 Hz, 3, CMe), 1.62 (s, 6, PdMe). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 137.7, 137.8, 134.9, 105.0, 104.8, 85.0 ($PdCH_2C{\equiv}$), 80.0 (${\equiv}C$Me), 19.7 (PdMe), 11.2 ($PdCH_2$), 5.08 (Me). Anal. Calc. for $C_{15}H_{21}BN_6Pd$: C, 44.75; H, 5.26; N, 20.87. Found: C, 44.52; H, 5.32; N, 20.38%.

2.1.2. $Pd(\overline{CH_2CH_2CH_2CH_2})(CH_2C{\equiv}CMe)\{(pz)_3BH\}$ (2)

A solution of $Pd(\overline{CH_2CH_2CH_2CH_2})$(tmeda) (0.038 g, 0.140 mmol) and $K[(pz)_3BH]$ (0.034 g, 0.140 mmol) in acetone (10 ml) was stirred for ca. 1 h at 0°C. 2-Butynyl bromide was added and a procedure identical to that for complex **1** gave a white solid (0.04. g, 57%). ^{1}H-NMR ($CDCl_3$): δ 7.80 (d, $^3J_{HH}$ = 3.0 Hz, 1, H3 or 5), 7.64 (d, $^3J_{HH}$ = 3.0 Hz, 1, H3 or 5), 7.59 (d, $^3J_{HH}$ = 3.0 Hz, 2, H3 or 5 *trans* to cycle), 6.20 (t, $^3J_{HH}$ = 3.0 Hz, 1, H4), 6.18 (t, 2, H4 *trans* to cycle), 3.38 (q, $^3J_{HH}$ = 9.0 Hz, 2, $PdCH_2CH_2$), 3.02 (q, $^3J_{HH}$ = 9.0 Hz, $PdCH_2CH_2$), 2.66 (q, $^5J_{HH}$ = 2.7 Hz, 2, $PdCH_2{-}C{\equiv}$), 1.83 (m, 4, $PdCH_2CH_2$), 1.78 (t,$^5J_{HH}$ = 2.7 Hz, 3, ≡CMe). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 137.3, 136.9, 133.5, 133.3, 103.3, 103.1, 83.0 ($PdCH_2C{\equiv}$), 49.9 ($PdCH_2$), 32.6 (CH_2CH_2), 11.7 ($C{-}CH_3$). Anal. Calc. for $C_{17}H_{23}BN_6Pd$: C, 47.64; H, 5.41; N, 19.61. Found: C, 47.73; H, 5.63; N, 19.91%.

2.1.3. $PtMe_2(CH_2C{\equiv}CMe)\{(pz)_3BH\}$ (3)

A solution of $[PtMe_2(SEt_2)]_2$ (0.035 g, 0.056 mmol) and $K[(pz)_3BH]$ (0.028 g, 0.110 mmol) in acetone (10 ml) was stirred for ca. 1 h at 0°C. 2-Butynyl bromide was added and the solution stirred overnight at 0°C to give a white precipitate. The solvent was evaporated in a vacuum to give a white oil which was dissolved in diethyl ether (10 ml) and centrifuged to remove insoluble KBr. The solution was separated from the solid, the volume reduced to ca. 4 ml in a vacuum and the product formed as a white solid on the addition of pentane (0.057 g, 68%). ^{1}H-NMR ($CDCl_3$): δ 7.70 (m,

3, H3 or 5), 7.53 (d, $^3J_{HH}=2.1$ Hz, 3, H3 or 5), 6.25 (m, 3, H4), 2.37 (q, $^2J_{PtH}=98.0$ Hz, $^5J_{HH}=2.8$ Hz, 2, $PtCH_2$), 1.69 (t, $^5J_{PtH}=21.3$ Hz, $^5J_{HH}=2.8$ Hz, 3, ≡CMe), 1.10 (s, $^2J_{PtH}=70.0$ Hz, 6, PtMe). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 137.8, 137.7, 135.7, 135.5, 106.1, 105.8, 84.6 ($CH_2-C\equiv$), 76.0 ($\equiv C-CH_3$), 4.7 ($\equiv C-CH_3$) −5.8 ($^2J_{PtC}=675$ Hz, PtMe), −10.8 ($^2J_{PtC}=690$ Hz, $PtCH_2$). Anal. Calc. for $C_{15}H_{22}BN_6Pt$: C, 36.67; H, 4.31; N, 17.11. Found: C, 36.59; H, 4.39; N, 17.06%.

2.1.4. $PdMe_2(CH{=}C{=}CH_2)\{(pz)_3BH\}$ (4)

The complex was obtained as a white solid by a similar procedure to that for complex **1**, using 2-propynyl bromide as oxidant (0.04 g, 87%). ^{1}H-NMR ($CDCl_3$): δ 7.68 (d, $^3J_{HH}=3.0$ Hz, 1, H3 or 5), 7.66 (d, $^3J_{HH}=3.0$ Hz, 2, H3 or 5 *trans* to PdMe), 7.58 (d, $^3J_{HH}=3.0$ Hz, 2, H3 or 5 *trans* to PdMe), 7.55 (d, $^3J_{HH}=3.0$ Hz, 1, H3 or 5), 6.24 (t, $^3J_{HH}=3.0$ Hz, 1, H4), 6.21 (t, $^3J_{HH}=3.0$ Hz, 2, H4 *trans* to PdMe), 5.80 (t, $^4J_{HH}=6.0$ Hz, 1, PdCH=), 4.53 (d, $^4J_{HH}=6.0$ Hz, 2, $=CH_2$), 1.70 (s, 6, PdMe). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 202.6 (=C=), 138.6, 138.1, 135.8, 135.3, 105.8, 105.6, 84.9 (PdCH=), 73.1 ($=CH_2$), 19.8 (PdMe). Anal. Calc. for $C_{14}H_{19}BN_6Pd$: C, 43.27; H, 4.93; N, 21.63. Found: C, 44.51; H, 4.89; N, 20.59%.

2.1.5. $Pd(CH_2CH_2CH_2CH)(CH{=}C{=}CH_2)\{(pz)_3BH\}$ (5)

Following a similar procedure to that followed for **2**, using 2-propynyl bromide as oxidant, the product was obtained as a white crystalline solid (0.03 g, 50%). ^{1}H-NMR ($CDCl_3$): δ 7.84 (d, $^3J_{HH}=3.0$ Hz, 1, H3 or 5, *trans* to allenyl), 7.67 (d, $^3J_{HH}=3.0$ Hz, 1, H3 or 5 *trans* to allenyl), 7.66 (d, $^3J_{HH}=3.0$ Hz, 2, H3 or 5), 7.54 (d, $^3J_{HH}=3.0$ Hz, 2, H4), 6.24 (t, $^3J_{HH}=3.0$ Hz, 1, H4 *trans* to allenyl), 6.19 (t, 2, H4), 5.91 (t, $^4J_{HH}=6.3$ Hz, 1, PdCH=), 4.56 (d, $^4J_{HH}=6.3$ Hz, 2, $=CH_2$), 3.47 (q, $^3J_{HH}=6.0$ Hz, 2, $PdCH_2$), 3.17 (q, $^3J_{HH}=6.0$ Hz, 2, $PdCH_2$), 1.82–1.88 (m, 4, CH_2CH_2). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 211.1 (=C=), 140.7, 137.6, 134.3, 104.0, 103.9, 78.1 (PdCH=), 75.1 ($=CH_2$), 52.3 ($PdCH_2$), 34.7 (CH_2CH_2). Anal. Calc. for $C_{16}H_{21}BN_6Pd$: C, 46.35; H, 5.10; N, 20.27. Found: C, 46.71; H, 5.51; N, 19.35%.

2.1.6. $PtMe_2(CH_2C{\equiv}CH)\{(pz)_3BH\}$ (6a) and $PtMe_2(CH{=}C{=}CH_2)\{(pz)_3BH\}$ (6b)

The complex was obtained as white solid by a similar procedure to that for complex **3**, using 2-propynyl bromide as oxidant, and with crystallisation achieved by addition of petroleum ether (b.p. 40–60°C) (87%). ^{1}H-NMR ($CDCl_3$): δ 7.72 (t, $^3J_{HH}=2.2$ Hz, 1, H3 or 5), 7.70 (t, $^3J_{HH}=2.8$ Hz, 2, H3 or 5 *trans* to PtMe), 7.63 (d, $^3J_{HH}=2.6$ Hz, 3, H3 or 5), 6.26 (m, 2, H4), 6.25 (m, 1, H4), 1.15 (s, $^2J_{PtH}=69.4$ Hz, 6, PtMe); propargyl isomer (**6a**): 5.76 (t, $^2J_{PtH}=105.0$ Hz, $^4J_{HH}=6.3$ Hz, 1, PtCH=), 4.24 (d, $^4J_{PtH}=44.6$ Hz, $^4J_{HH}=6.3$ Hz, 2, $=CH_2$); allenyl isomer (**6b**): 2.43 (d, $^2J_{PtH}=103.8$ Hz, $^4J_{HH}=3.0$ Hz, 2, $PtCH_2$), 2.16 (t, $^4J_{PtH}=19$ Hz, $^4J_{HH}=2.7$ Hz, 1, ≡CH); ratio of isomers **6a**:**6b** = 3:2. $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 137.7.7, 137.6, 135.8, 135.9, 106.0, 105.1, −5.4 (PtMe). Insufficiently stable for microanalysis.

2.1.7. $PdBrMe_2(CH_2C{\equiv}CMe)(bpy)$ (7)

2-Butynyl bromide (15 μl) was added to a solution of $PdMe_2(bpy)$ (0.048 g, 0.163 mmol) in acetone (5 ml) at −30°C and the solution stirred for 20 min. A pale yellow solid formed, separated by decantation, and the solvent was evaporated in a vacuum. The residue was dissolved in dichloromethane and a white solid formed on addition of petroleum ether (b.p. 40–60°C) (0.058 g, 76%). ^{1}H-NMR ($CDCl_3$, −20°C): δ 8.83 (d, $^3J_{HH}=4.6$ Hz, 2, H6), 8.20 (d, $^3J_{HH}=8.4$ Hz, 2, H3), 7.99 (m, 2, H4), 7.60 (m, 2, H5), 2.17 (q, $^5J_{HH}=2.7$ Hz, 2, $PdCH_2$), 1.94 (s, 6, PdMe), 1.20 (t, $^5J_{HH}=2.8$ Hz, 3, CMe), together with a resonance attributed to ethane (0.86 ppm). Insufficiently stable for ^{13}C-NMR or microanalysis.

2.1.8. $PtBrMe_2(CH_2C{\equiv}CMe)(bpy)$ (8)

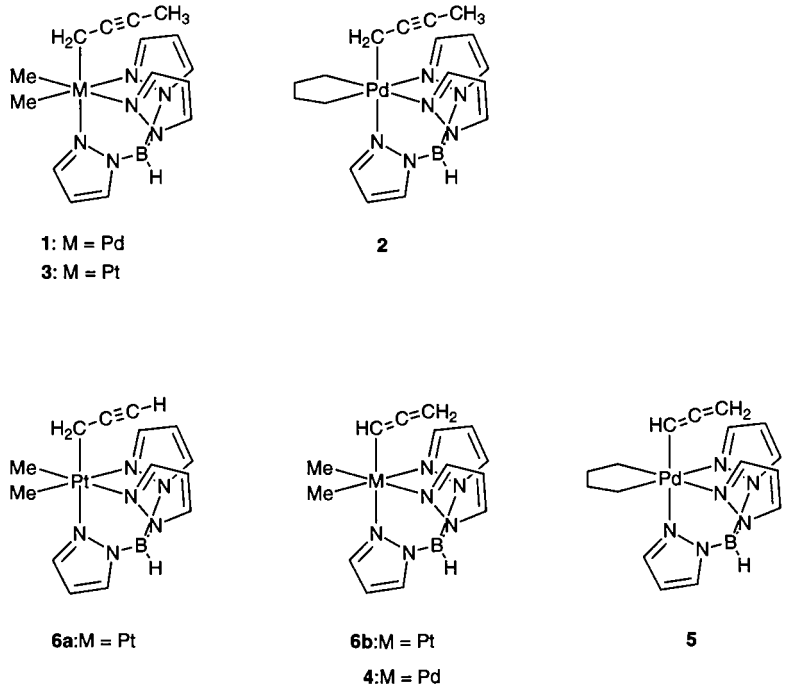
2-Butynyl bromide (15 μl) was added to a solution of $PtMe_2(bpy)$ (0.047 g, 0.123 mmol) in dichloromethane (3 ml) and the solution stirred for 30 min. The volume was reduced to ca. 1 ml in a vacuum and diethyl ether added to crystallise the product. A pale yellow solid was collected, washed with diethyl ether and dried in a vacuum (0.038 g, 60%). ^{1}H-NMR ($CDCl_3$): δ 8.93 (dd,$^3J_{HH}=5.7$ Hz, 2, H6), 8.23 (d, $^3J_{HH}=8.1$ Hz, 2, H3), 8.05 (m, 2, H4), 7.65 (m, 2, H5), 1.83 (q, $^2J_{PtH}=93.3$ Hz, $^5J_{HH}=2.8$ Hz, 2, $PtCH_2$), 1.46 (t, $^2J_{PtH}=69.6$ Hz, 6, PtMe), 1.10 (t, $^5J_{PtH}=25.3$ Hz, $^5J_{HH}=2.8$ Hz, 3, CMe). $^{13}C\{^1H\}$-NMR ($CDCl_3$, low solubility): δ 147.9 ($J_{PtC}=3.2$ Hz), 126.9, 139.0, 123.4, 157.3, −3.32 (PtMe). Anal. Calc. for $C_{16}H_{19}BN_2Pt$: C, 37.37; H, 3.72; N, 5.45. Found: C, 37.46; H, 3.82; N, 5.36%.

2.1.9. ^{1}H-NMR study of the reaction of $PdMe_2(bpy)$ with 3-propynyl bromide: detection of unstable $PdBrMe_2(CH_2C{\equiv}CH)(bpy)$ (9)

A solution of $PdMe_2(bpy)$ (0.080 g, 0.027 mmol) in acetone-d_6 was cooled to −20°C in an NMR tube. An excess of 2-propynyl bromide (3 μl, 0.040 mmol) was added and spectra obtained at 10 min intervals until the palladium(II) reagent had been consumed (ca. 90 min). ^{1}H-NMR ($CDCl_3$): δ 8.88 (d, $^3J_{HH}=5.0$ Hz, 2, H6), 8.66 (d, $^3J_{HH}=7.9$ Hz, 2, H3), 8.25 (m, 2, H4), 7.81 (m, 2, HS); propargyl group *trans* to bromine (**9a**): 1.98 (2, $^4J_{HH}=2.7$ Hz, 2, $PdCH_2$), 1.89 (s, 6, PdMe), 1.36 (m, 1, ≡CH); propargyl group *trans* to bpy (**9b**): 2.09 (d, $^4J_{HH}=2.9$ Hz, 2, $PdCH_2$), 1.75 (s, 3, PdMe *trans* to bpy), 1.34 (m, 1, ≡CH), 0.96 (s, 3, PdMe *trans* to Br); ratio **9a**:**9b** = 2:1.

2.1.10. $PtBrMe_2(C_3H_3)(bpy)$ (10)

2-Propynyl bromide (12 μl, 0.16 mmol) was added to



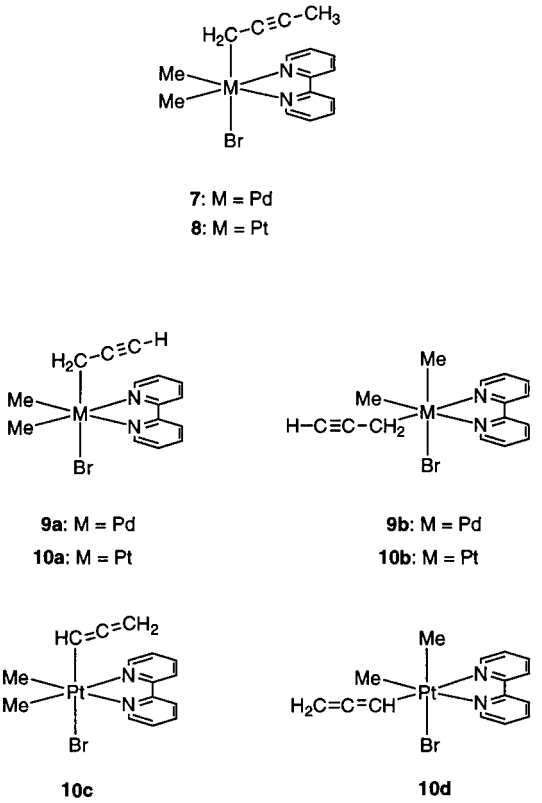
Scheme 1.

a solution of $PtMe_2$(bpy) (0.056 g, 0.147 mmol) in dichloromethane (3 ml) and the solution stirred for 2 h. The volume of the pale yellow solution was reduced to ca. 1 ml and diethyl ether added to precipitate the product which was collected and washed with diethyl ether (0.042 g, 60%). ^{1}H-NMR ($CDCl_3$): δ 8.90 (m, 1, H6), 8.23 (d, $^3J_{HH} = 8.0$ Hz, 2, H3), 8.04 (m, 2, H4), 7.65 (m, 2, HS); allenyl group *trans* to bromine (**10a**): 5.08 (d, $^2J_{PtH} = 64.6$ Hz, $^4J_{HH} = 6.2$ Hz, 1, CH=), 3.50 (d, $^4J_{PtH} = 52.2$ Hz, $^4J_{HH} = 6.2$ Hz, 2, C=CH_2), 1.48 (s, $^2J_{PtH} = 69.6$ Hz, 6, PtMe); allenyl group *trans* to bpy (**10b**): 6.64 (t, $^2J_{PtH} = 125$ Hz, $^4J_{HH} = 6.2$ Hz, 1, PtCH=), 4.40 (d, $^4J_{PtH} = 44.3$ Hz, $^4J_{HH} = 6.3$ Hz, 2, C=CH_2), 1.55 (s, $^2J_{PtH} = 68.9$ Hz, 3, PtMe *trans* to bpy), 0.82 (s, $^2J_{PtH} = 74.4$ Hz, 3, PtMe *trans* to bromine); propargyl group *trans* to bromine (**10c**): 2.23 (t, $^4J_{PtH} = 21.5$ Hz, $^4J_{HH} = 2.9$ Hz, 1, ≡CH), 1.85 (d, $^2J_{PtH} = 95.7$ Hz, $^4J_{HH} = 2.8$ Hz, 2, $PtCH_2$), 1.49 (s, $^2J_{PtH} = 69.6$ Hz, 6, PtMe); propargyl group *trans* to bpy (**10d**): CH_2–C≡CH resonances obscured, 1.53 (s, $^2J_{PtH} = 68.9$ Hz,3, PtMe *trans* to bpy), 0.78 (s, $^2J_{PtH} = 73.8$ Hz, 3, PtMe *trans* to bromine); ratio **10a**:**10b**:**10c**:**10d** = 18:1:9:6. ^{13}C-NMR ($CDCl_3$, low solubility): δ 154.7, 123.8, 139.3, 127.3, 147.6.

3. Results and discussion

The reagents MMe_2(bpy) (M = Pd, Pt) are readily available [42,45,46] and the diorgano{tris(pyrazol-1-yl)borato}metal(II) reagents were obtained by displacement of tmeda or diethylsulphide from $PdMe_2$(tmeda), $Pd(CH_2CH_2CH_2CH_2)$(tmeda) or $[PtMe_2(SEt_2)]_2$ [48,49]. The reactivity of metal(II) precursors with HC≡C–CH_2Br or MeC≡C–CH_2Br was examined by ^{1}H-NMR spectroscopy at low temperature followed by successful isolation of complexes for all except **9** which was not attempted owing to its low stability (Reactions 2–4). The structures of all complexes, including mixtures of tautomers for **6**, **9** and **10**, and isomers for **9** and **10**, are shown in Schemes 1 and 2.

^{1}H-NMR spectra of the isolated complexes (**1–8**, **10**) and the unstable complex detected in solution (**9**) may be readily assigned and are in accord with the formulations presented in Schemes 1 and 2. The propargyl and allenyl groups exhibit characteristic spectra, as illustrated for complex **6** in Fig. 1. For example, although $^2J_{PtH}$ coupling for the Pt–CH_2–C≡CH (103.8 Hz) and Pt–CH=C=CH_2 (105.0 Hz) groups of **6a** and **6b** are similar, presence of the former resonance as a doublet ($^4J_{HH} = 2.9$ Hz) and the latter as a triplet ($^4J_{HH} = 6.3$ Hz) clearly indicate propargyl and allenyl formulations, respectively. For complexes **9** and **10** (Scheme 2) similar approaches allow assignment of propargyl and allenyl functionality, and the chemical shifts and integrals for PtMe resonances indicate orientation of methyl groups *trans* to bpy or bromine. Thus, complex **9** exhibits PdMe resonances at 1.89, 1.75 and 0.96 ppm in a 12:3:3



Scheme 2.

ratio where the high field resonance is characteristic of a methyl group *trans* to a halogen ($PdIMe_3(bpy)$ has resonances at 1.85 and 1.14 ppm in 2:1 ratio in the same solvent [50]), indicating occurrence of structures **9a** and **9b** in a 2:1 ratio. Integration for propargyl resonances of **9a** and **9b** are consistent with this assignment, and for the related platinum(IV) complexes **10a–d** additional support is obtained from $^2J_{PtH}$ values, e.g. **10a** and **10b** exhibit PtMe resonances at 1.48 ($^2J_{PtH} = 69.6$ Hz) (**10a**), 1.55 ($^2J_{PtH} = 68.9$ Hz) (**10b**) and 0.82 ppm ($^2J_{PtH} = 74.4$ Hz) (**10b**) where the high field resonance corresponds to the methyl group *trans* to bromine.

Satisfactory microanalysis could not be obtained for complexes **6**, **7** and **10** which have low stability, and the very unstable complex **9** exhibits a resonance for ethane in ^{1}H-NMR spectra at -20°C indicating the occurrence of reductive elimination. Even for the more stable complexes, low stability to heating prevented studies of the possible interconversion of tautomers and isomers in solution.

The reagent $MeC{\equiv}C{-}CH_2Br$ retains its propargyl functionality on formation of the metal(IV) complexes **1–3**, **7** and **8**, in contrast to related metal(II) chemistry where $MeC{\equiv}C{-}CH_2Cl$ reacts with $Pt(PPh_3)_4$ to form the allenyl complex *trans*-$PtCl(CH{=}C{=}CHMe)(PPh_3)_2$ [9], and $MeC{\equiv}C{-}CH_2Br$ reacts with $Pd(PPh_3)_4$ to form an allenyl/propargyl mixture, *trans*-$PdBr(CH_2C{\equiv}CMe)(PPh_3)_2$ and *trans*-$PdBr(CH{=}C{=}CH_2)(PPh_3)_2$ [6]. Using $HC{\equiv}C{-}CH_2Br$ as an oxidant for metal(II) complexes, extensive tautomerism is observed for the metal(IV) products **4–6**, **9** and **10**: propargyl/allenyl for Pt(IV) in **6** but allenyl only for Pd(IV) in **4** and **5**, propargyl/allenyl for Pt(IV) in **10** but propargyl only for Pd(IV) in **9**. In contrast, the most closely related metal(II) complexes occur in the allenyl form in *trans*-$PtX(CH{=}C{=}CH_2)$-

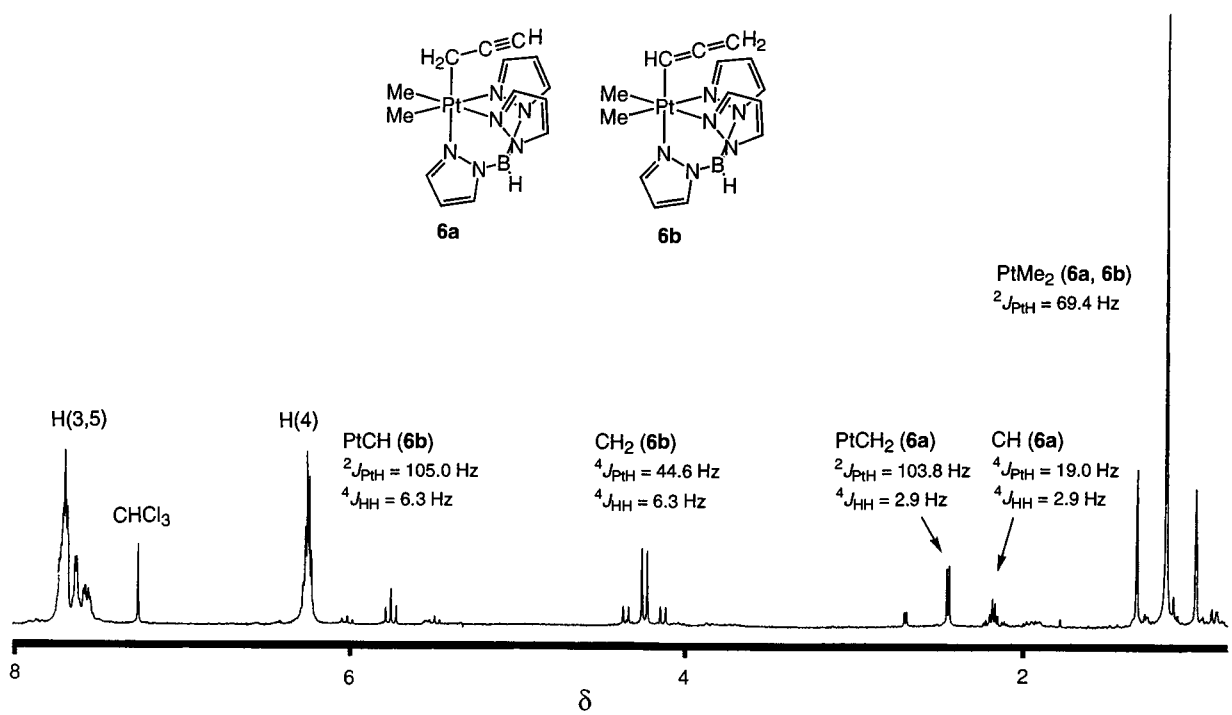


Fig. 1. ^{1}H-NMR spectra for the tautomers **6a** and **6b**.

$(PPh_3)_2$ (X = Cl [10], Br [9]), [Pt(CH=C=CH_2)(en)(P-$Ph_3)_2$]Br (en = ethylenediamine) [14] and *trans*-PdX(C-H=C=CH_2)$(PPh_3)_2$ (X = Cl [5], Br [3]).

It is difficult to draw firm conclusions from these observations for metal(IV) complexes, except that the preference for propargyl and allenyl tautomers is finely balanced and dependent upon the metal, ancillary ligands, and substitution in the propargyl/allenyl fragments M–C_3H_3 and M–C_3H_2Me. Thus, for M–C_3H_2Me propargyl is favoured, and for M–C_3H_3 allenyl is favoured for the Pd(IV)/$[(pz)_3BH]^-$ substrates but propargyl is favoured for the Pd(IV)/bpy substrate.

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